ATOMIC- AND DEVICE-SCALE PHYSICS OF ION-TRANSPORT MEMRISTORS

Arthur Edwards

2 Feb 2017

Interim Report

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

This effort has been de-emphasized during the last year after the AFOSR program manager indicated they were interested in redirecting research toward wide- and ultra-wide-band gap semiconductor research. Our redirection has led to successful AFOSR proposal on defects in GaN and AlN. We also made some progress on the theory of metal motion and incorporation in Ge_2Se_3, the activation energy for silver and copper motion in crystalline SiO_2, and the electronic structure of copper in Ge_2Se_3. Finally, our graduate student has finished writing his MS thesis on oxygen in Ge_2Se_3.

15. SUBJECT TERMS

Ion Transport, Memristors, GaN, AlN

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I. INTRODUCTION

Conductive bridge memristors, wherein metal ions traverse an electrolyte under positive bias to deposit onto a bottom electrode, and, hence, build conductive, metallic dendrites, are of continuing technological relevance. Several academic institutions, including Arizona State University, Boise State University, and University of Michigan, continue to pursue the technology for applications in non-volatile memory, neuromorphic computing, and even physically unclonable functions (PUF's). In addition, Adesto is selling devices with embedded memristors that exploit this technology. Our internal interest in this technology arises from both a need for high denisty, radiation hard nonvolatile memory, and from our understanding that our long-term requirements for very low power, high performance space computation, could well be satisfied using neuromorphic/cortical architectures that rely on these devices. Air Force Office of Scientific Research (AFOSR) has indicated a hange in direction of the portfolio from theoretical work on memristors, to the science of wide- and ultra wide-band gap semiconductors. As a result, a significant part of our in-house effort was spent on an Innovative Research Proposal (IRP) that was awarded last year in the same area. The result of our redirection is a new AFOSR laboratory research initiative request (LRIR) that was just funded at the beginning of December. However, we have still made some significant progress on the physics of metal ions in conductive bridge memristors that we will report here. We have broadened our effort to include SiO_2 as an active layer material, and we have also broadened our scope to include copper, along with silver. Most importantly, however, we have finally succeeded in discovering the reaction path for an interstitial metal ion to replace germanium. This reaction path had been posited by Campbell and coworkers, and we have long had theoretical results that supported this from a thermodynamic perspective. However, we now have activation energies, so that we can discuss the kinetics.

II. METHODS

The bulk of our work has been modeling, using density functional theory (DFT). We are using QUEST, a local orbital code that uses a highly converged (triple-zeta quality) Gaussian basis set. It calculates total energies in a variety of approximations, including local density

and generalized gradient, and it can use spin-unrestricted formalism. It calculates equilibrium geometries, and can find activation energies using the nudged elastic band method [1]. For charged defects, we have used the standard *jellium* approximation, and we have used the Jost approximation to account for long-range polarization effects [2]. In most of our work, we have used an 80 atom supercell based on a crystalline model derived from Si_2Te_3 [3], shown in Figure 1. This supercell has been re-optimized for Ge_2Se_3, and the calculated
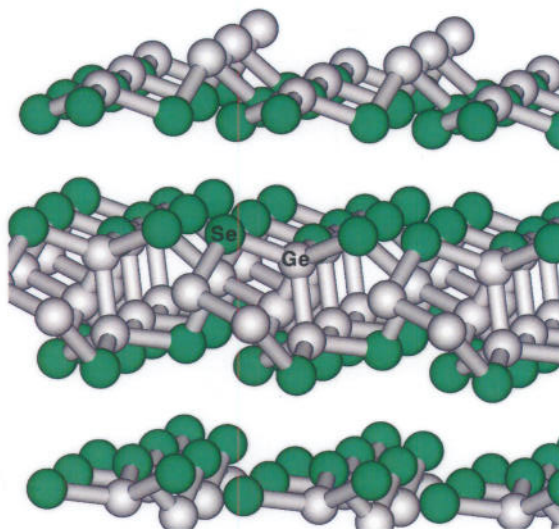

Figure 1: Model system used for Ge_2Se_3. Atomic species are labeled.

local arrangement agrees with both experiment (Extended X-Ray Absorption Fine Structure (EXAFS) [4]), and molecular dynamics simulation [5] for glassy Ge_2Se_3, where both predict that each germanium atom is, on average, surrounded by three selenium atoms and on germanium atom, and that each selenium atom is surrounded by two germanium atoms. The presence of a large density of germanium dimers determines much of the behavior of metal ions in this material. For calculations in SiO_2, we have used a 72 atom unit cell for crystalline calculations, and a 192 atom amorphous cell. In each case, we expect significant variations from our results due to disorder. However, we also expect that local chemistry will dominant, so that the insight we gain will be relevant.

III. RESULTS

A. Silver incorporation into the Ge$_2$Se$_3$ network.

We have reported before on the electronic structure of Ge$_2$Se$_3$[6, 7] and of silver and tin in Ge$_2$Se$_3$ [8]. Of particular interest are the results for silver incorporation, shown in Figure 2, taken from reference [8]
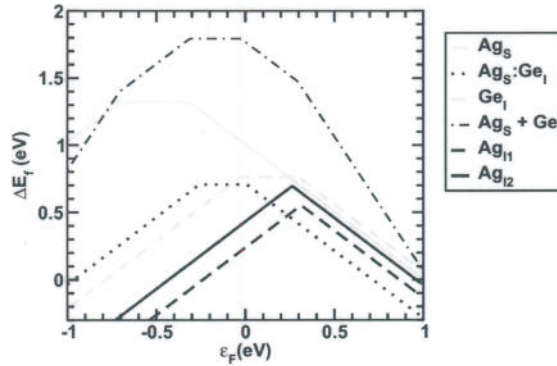

Figure 2: Energies of formation for various structures containing silver in Ge$_2$Se$_3$.

The zero of ϵ_F is the Fermi level in the ideal bulk. Near that value, the lowest energy configuration is interstitial silver. However, even at that Fermi energy, the configuration with silver replacing germanium, and the germanium in a neighboring interstitial position (Ag$_{sub}$:Ge$_{int}$), shown in Figure 3, is only ~0.4 eV higher in energy. This reflects the weakness of the Ge-Ge bond. For a Fermi energy a few tenths of an eV above the ideal bulk value, the Ag$_{sub}$:Ge$_{int}$ conformation is lower in energy than interstitial silver. While this is interesting thermodynamically, its technological relevance will depend on kinetics. Put simply, does this reaction occur with great enough frequency to play a role in building metallic silver dendrites? We have struggled to find a viable reaction path between the two conformations. However, recently, we returned to some very early calculations in which we inserted silver between two germanium atoms and let the system relax. The result is shown in Figure 4, where it is clear the the dimer atoms were pushed through the plane of their nearest neighbor selenium atoms. When we considered just the energy to rupture the Ge-Ge bond in the absence of silver, we found this to be a surprisingly low energy reaction. We were successful in finding a viable reaction path when we started with an initial guess (reaction path) where the first event was a one-sided rupture in which one of the germanium atoms
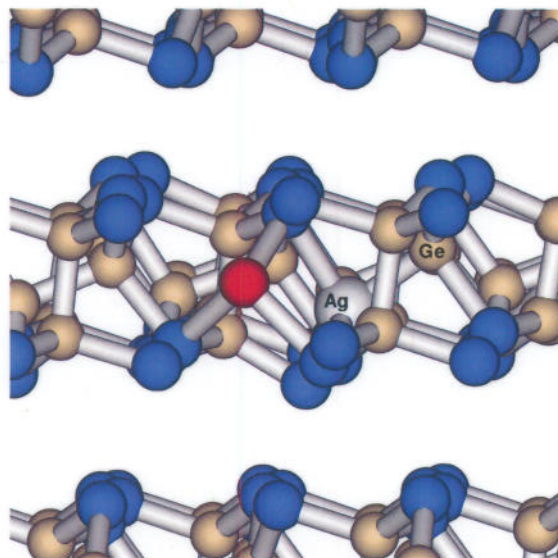
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Figure 3: Equililbrium structure of the silver substitutional, germanium interstitial defect. Interstitial germanium is in red for clarity.

puckered through the plane of its three neighbors, after which the silver atom replaces it on the substitutional site. After the system relaxed, we found that the activation energy for this reaction was ˜0.75 eV. This results can now be included in a kinetic Monte Carlo simulation.

B. Silver and copper in Ge_2Se_3 and SiO_2

Our colleagues at ASU have been pursuing new materials systems, including copper and silver in amorphous silicon dioxide. They have found significant differences in ion transport. We have argued previously that in Ge_2Se_3 silver will auto-ionize– that the highest occupied atomic level, the $5s$-state, is above the conduction band edge, so the electron will drop to that band edge, leaving the silver ion positively charged. Because SiO_2 has a much larger band gap, it was not clear that the same physics would apply. We have calculated the equilibrium geometry in both crystalline α-quartz and in an amorphous model developed by Sushko and Schluger [9]. In both systems, all atoms have satisfied valence. In the amorphous structure there is considerable variation in bond lengths and bond angles. We have also performed similar calculations on copper in Ge_2Se_3. The results are shown in Figure 5. Note that neither copper nor silver have states in the gap. In fact, the last occupied atomic state,
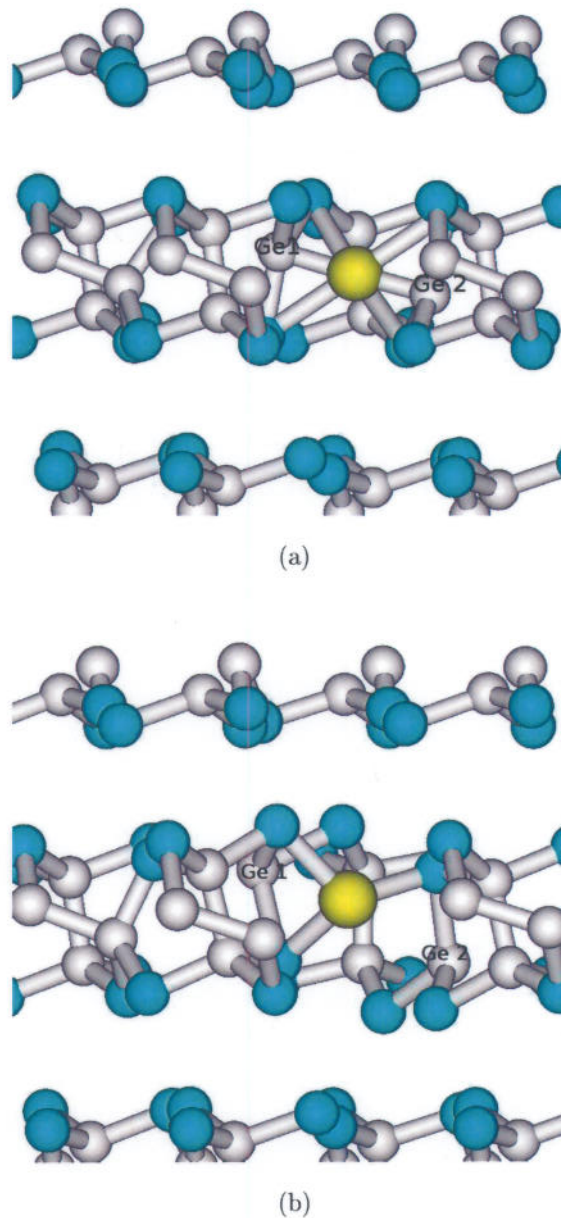
(a)

(b)

Figure 4: Silver insertion between two germanium atoms. (a) initial guess (b) final conformation. Germanium in grey, selenium in blue, silver in yellow. The two germanium atoms of interest are labeled in each figure.

$4s$ for copper and $5s$ for silver, are above the conduction band, leading to spontaneous ionization. However, in SiO_2, with a Kohn-Sham gap of ~6.2 eV, the $4s$ state for copper and the $5s$ for silver are in the band gap, implying that there are conditions under which both silver and copper can enter SiO_2 as neutral atoms, or they can trap electrons. That there are
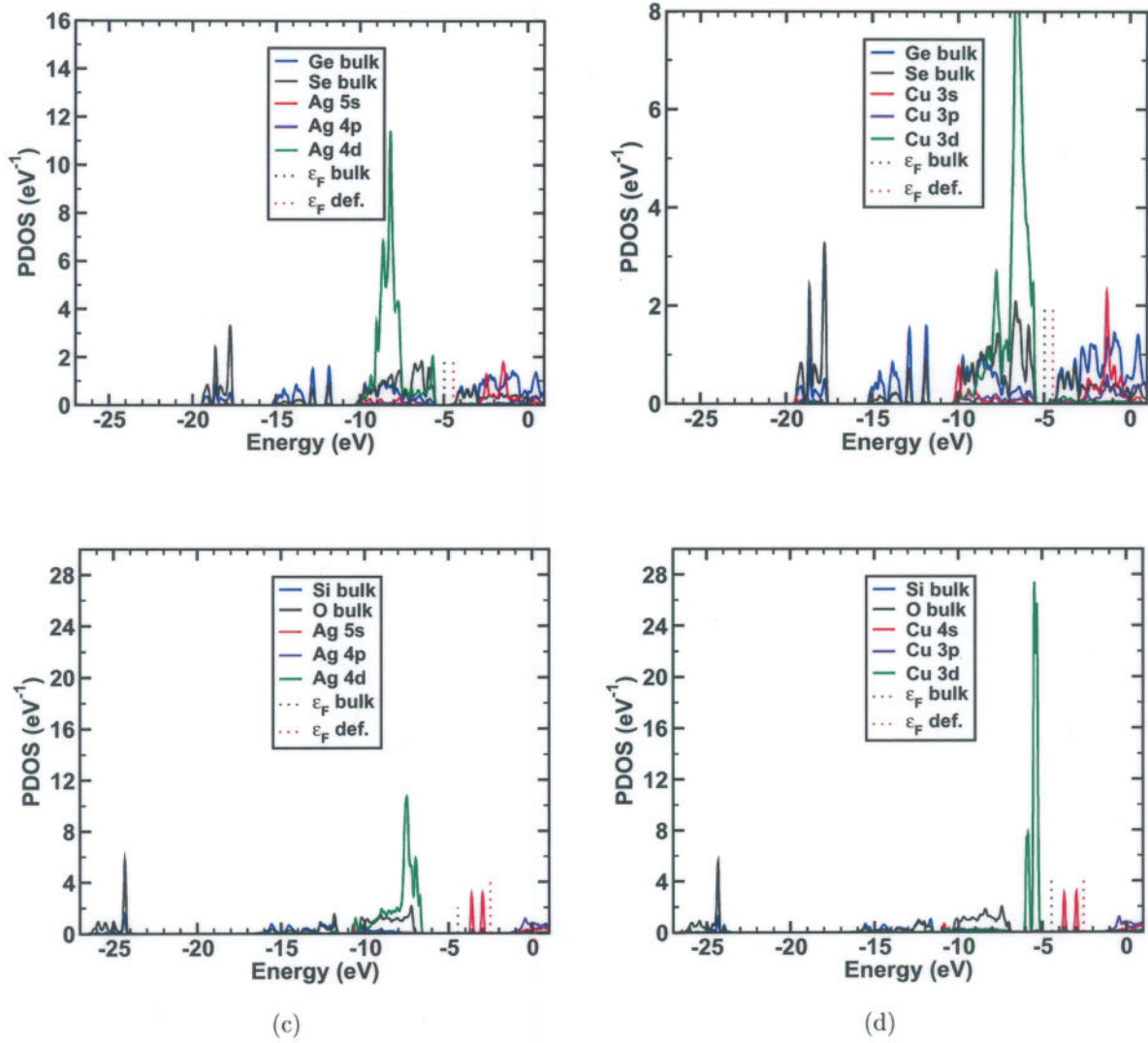
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Figure 5: Projected density of states (PDOS) for Ag and Cu in Ge_2Se_3 and SiO_2. (a) Ge_2Se_3:Ag, (b) Ge_2Se_3:Cu, (c) SiO_2:Ag, (d) SiO_2:Cu.

two s-like peaks in the gap for both copper and silver, and two d-like peaks for copper merely reflects that these are spin-unrestricted calculations and that, in each case, the lower peak is occupied, while the upper peak is not. Note an important difference between copper and silver in SiO_2: the copper d-states give rise to a strongly localized state completely within the band gap, so that we expect copper to be potentially positively charged. Neither is the case in Ge_2Se_3. We have calculated electrical levels for both copper and silver in SiO_2. They reflect the PDOS shown in Fig 5. Copper becomes neutral when ϵ_F ristes 1.8 eV above the crystalline Fermi level. It becomes doubly positively charged when ϵ_F is 2.2 eV *below* the

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bulk Fermi level. Silver only has two charge states in the gap. It is predicted to be in the $+1$ charge state unless ϵ_F is ~2.8 eV above the bulk Fermi level. So, for ϵ_F near the bulk value, both copper and silver are positively charged, so that at low densities, we would expect field driven transport. However, in radiation experiments, where large densities of electron-hole pairs are present, both of these ions can trap electrons and become neutral, and so they will not participate in field driven transport. Finally, we have calculated activation energies for Cu^{+1} and Cu^{+2} in α-quartz. These calculations are for either charge state moving along the c-axis assuming a purely interstitial transport. The activation energies are 0.06 eV, and 0.37 eV, respectively. So, in either charge state, copper is predicted to be a very fast diffuser.

IV. FUTURE WORK

As AFOSR has moved in a different direction, we will be de-emphasizing work on memristors. We have several manuscripts to write, including a manuscript on silver clustering, and a peer-reviewed version of reference [8]. We also have at least one manuscript from our student's thesis. We will submit a proposal to the AFRL HPC for time so that we can pursue more work on the kinetics of metal ions in SiO_2 and in other germanium-selenium compounds, such as $GeSe_2$. All of this will be subordinated to the new, funded work on GaN/AlN.

V. PUBLICATIONS

We have seven publications, including a review in the Proceedings of the IEEE. They are given in the bibliography as Refs. [10–16]. We also given invited presentations at Boise State University, Arizona State University, and New Mexico State University.

VI. ACRONYMS

1. AFOSR Air Force Office of Scientific Research

2. DFT density functional theory

3. EXAFS Extended X-ray absorption fine structure

4. LRIR laboratory research initiative request

5. PDOS Projected density of states

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